# Modelling the Effects of Doping in Argyrodite Solid Electrolytes using Machine Learning Methods

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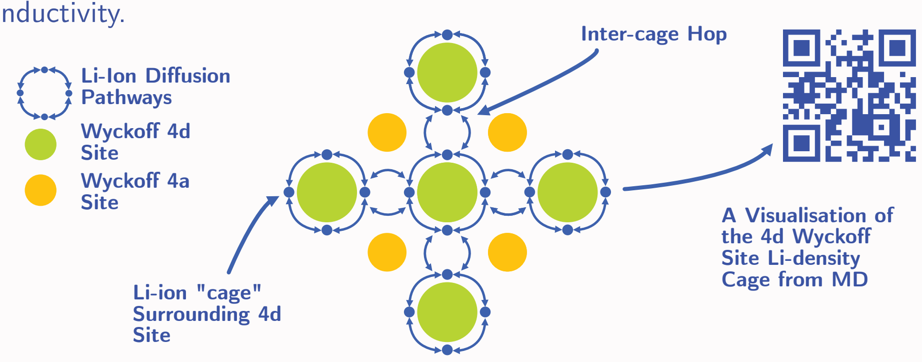
## Introduction

**Halide lithium argyrodites** ($Li_6PS_5X$ , X = **Cl**, **Br**, **I**) are a promising class of **solid-state electrolytes** for next-generation batteries, achieving room-temperature ionic conductivities of **$10^{-3}$–$10^{-2}$ Scm$^{-1}$** with comparatively wide electrochemical stability windows.

Argyrodites show strong chemical tunability[1]: most prominently, **anion disorder** between **4a ($X^-$)** and **4d ($S^{2-}$)** sites enhances Li-cage connectivity and lowers migration barriers[2]; secondly, introducing Li vacancies (via **aliovalent doping** or off-stoichiometry) enables vacancy-assisted transport, further boosting conductivity.



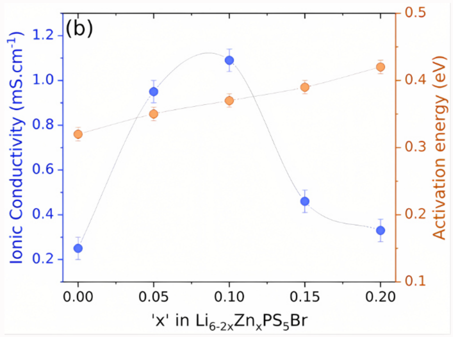
## Motivation

**Doping $Zn^{2+}$ ...**

**Increases Disorder:** **Increases Conductivity**

**Increases Vacancies:** **Increases Conductivity**

**Increases Zinc:** **Decreases Conductivity?**

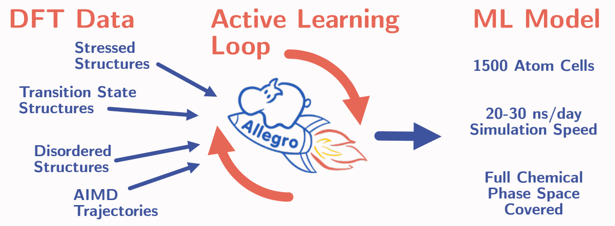


**Recent work** has found that **$Zn^{2+}$ addition** to the argyrodite $Li_{6-2x}Zn_xPS_5Br$ **increases 4a/4d disorder - boosting $Li^+$-ion conductivity**. However, excessive $Zn^{2+}$ addition **decreases conductivity**, consistent with suspected $Zn^{2+}$- induced blocking on the $Li^+$ sub-lattice.

The atomic-scale mechanism - and the precise origin of this suspected blocking - remains unresolved.

## Methods

To correctly simulate disorder-driven dynamics with molecular dynamics over a vast compositional/configurational space an **Allegro**[3] machine learnt interatomic potential was trained and deployed. Training datasets were generated across the compositional phase space and the model refined via an **active-learning loop** - delivering *ab initio* fidelity at practical computational cost.



**DFT Data**
- Stressed Structures
- Transition State Structures
- Disordered Structures
- AIMD Trajectories

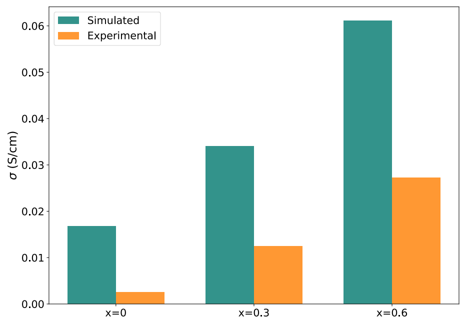
**Active Learning Loop**

**ML Model**
- 1500 Atom Cells
- 20-30 ns/day Simulation Speed
- Full Chemical Phase Space Covered

## References

1. Morgan, B. *J. Chem. Mater.* **2021**, 33, 2004
2. Gautam, A et al. *Advanced Energy Materials*. **2021**, 11, 2003369.
3. Musaelian A et al. *Nature Communications*. **2023** 14, 579.
4. Shanbhag, D et al. *Journal of Power Sources*. **2025**, *657*, 238175.
5. Lavrinenko, A. K et al. *J. Mater. Chem. A*. **2024**, 12, 26596.

## $Li_{6-x}PS_{5-x}BrCl_x$: an un-doped system



Methods were validated on $Li_{6-x}PS_{5-x}BrCl_x$ before Zn was introduced.

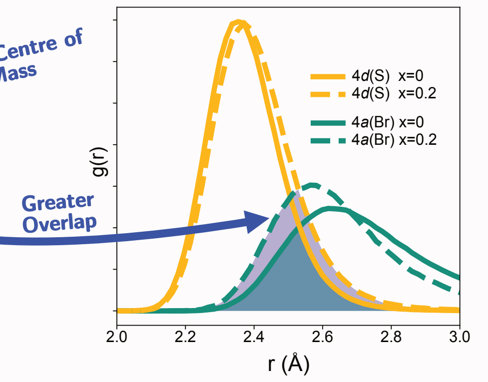
With increasing halide content, the system becomes more **Li-poor** and **exhibits greater 4a/4d site disorder**. Given the strong correlations in these systems, the **dc conductivity** is computed via **linear-response theory** finding good agreement with experiment.

$$\sigma_{\mathrm{dc}} = \frac{e^2}{6\,k_B T\,V} \lim_{t\to\infty} \frac{d}{dt} \left\langle \left|\Delta \mathbf{R}_{\mathrm{Li}}(t)\right|^2 \right\rangle$$

**Li-ion Centre of Mass**

As **x** increases, **4a(Br) cages harden** and compress, resembling the unchanged 4d cages, yielding a **more uniform $Li^+$ distribution**[4].

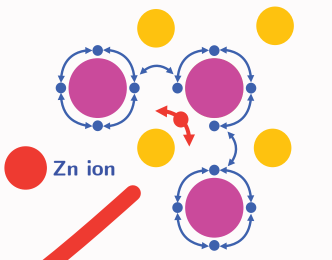
This homogenisation, removes cage-specific bottlenecks and enables smoother, more continuous Li-ion pathways[5] - **improving conductivity.**



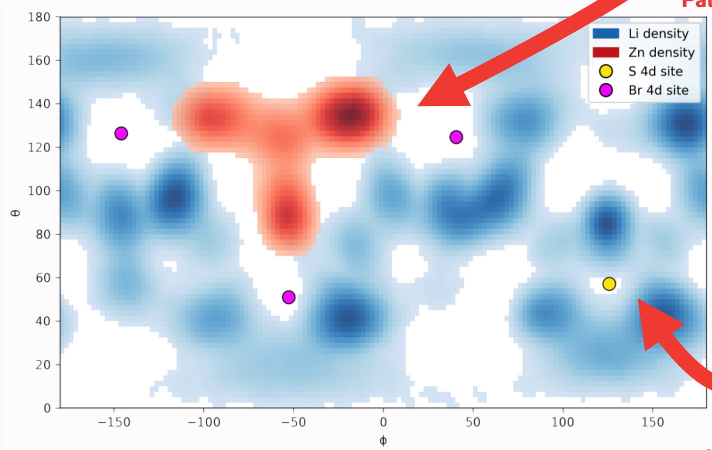
## $Li_{6-2x}Zn_xPS_5Br$: zinc doping

$Zn^{2+}$ **repels $Li^+$** and **moves via Br-centred 4d sites**, where it sits at larger Zn–Br separations that enable 4d→4d (Br→Br) hopping.

**Increasing 4a/4d disorder**:
- **More Br on 4d**
- **$Zn^{2+}$ is more mobile**
- **$Zn^{2+}$ increasingly blocks transport**



**Zn Blocking 4d/Br Diffusion Pathways!**



**The radially - projected $Li^+$ and $Zn^{2+}$ density around a 4a site showing Zn moving 4d→4d (Br→Br) and blocking Li transport pathways**

**No Zinc Movement Near 4d/S Sites**

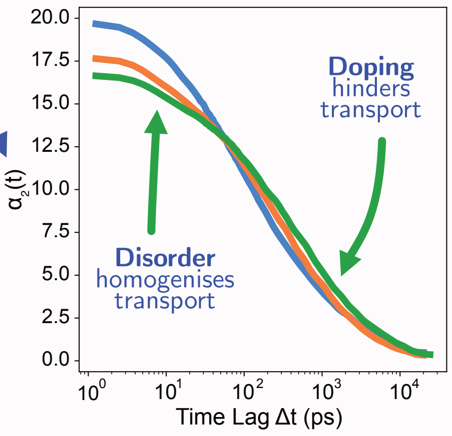
**Dynamically:**

**A Measure of Dynamic Heterogeneity**

**Disorder** reduces diffusive bottlenecks at shorter timescales - **increasing conduction**.

**Vacancies promote conduction** seen by in an increased ion hop frequency on Zn containing 4d(Br) sites.

**Zn2+** blocks diffusion pathways more as **Zn2+ concentration** and **disorder increase - decreasing conductivity**.



**Doping** hinders transport

**Disorder** homogenises transport

More mobile $Zn^{2+}$ **persistently blocks $Li^+$ pathways**, compounding the suppression of $Li^+$ transport and **offsetting** the gains expected from **increased $Li^+$-vacancy concentration** and **more uniform** $Li^+$ **density**.

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